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CATEGORIZATION (LISTING) BACKGROUND DOCUMENT

2-NITROPROPANE

(CAS: 79-46-9)

ONTARIO MINISTRY OF THE ENVIRONMENT

WASTE MANAGEMENT BRANCH

HAZARDOUS WASTE REVIEW UNIT

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TABLE OF CONTENTS

1.0 SUMMARY OF BASIS FOR CATEGORIZATION 1
1.1 Listing under Regulation 309 1
1.2 Listing under other Canadian legislation 1
1.3 Listing under U.S. legislation 2

2.0 DESCRIPTION OF INDUSTRIAL SECTOR 2
2.1 Production of 2-Nitropropane 2
2.2 Use in the chemical industry 3
2.3 Use as a solvent/reagent 3
2.3.1 Production and use of printing ink 3

3.0 WASTE MANAGEMENT PRACTICES 4
3.1 Waste Generation 4
3.1.1 Ink production and use 4
3.2 Waste management 5

4.0 HAZARDOUS PROPERTIES OF THE WASTE 5
4.1 Hazardous properties 5
4.2 Hazardous characteristics 5
4.3 Physical and chemical properties 6
4.4 Environmental behaviour 6
4.4.1 Environmental mobility 6
4.4.2 Persistence 6
4.4.3 Bioaccumulation 6
4.4.4 Environmental Exposure 7
4.5 Toxicity 7
4.5.1 Acute lethality 7
4.5.2 Sublethal effects, plants 7
4.5.3 Sublethal effects, mammals 8
4.5.4 Sublethal effects, non-mammalian 8
4.5.5 Teratogenicity 8
4.5.6 Mutagenicity 8
4.5.7 Carcinogenicity 9
4.6 Results of Vector Scoring 9

5.0 CONCLUSIONS AND RECOMMENDATIONS 9

6.0 REFERENCES 14

Appendix A: U.S. Regulations
B. Justification for Vector Scores of 2-Nitroopropane
C. Proposed Amendment to Regulation 309

LIST OF TABLES

TABLE PAGE

1. Ontario printing ink formulation establishments reporting to Statistics Canada 10

2. Estimated 1987 generation of 2-nitropropane waste in Ontario 11

3. Properties of 2-nitropropane 12

4. Results of vector scoring of 2-nitropropane 13

1.0 SUMMARY OF BASIS FOR CATEGORIZATION

1.1 Listing under Regulation 309

The Ontario Ministry of the Environment (M.O.E.) is considering amending Regulation 309 and listing 2-nitropropane in Schedule 1 as a hazardous industrial waste.

This listing would be achieved as follows:

> 2-Nitropropane waste would be listed as a hazardous industrial waste in Schedule 1, (paragraph NA9305), when a 2-nitropropane mixture is disposed of as a spent solvent, or when the still bottoms from the recovery of the spent solvent are disposed of as a waste.
>
> 2-Nitropropane is already listed in Schedule 2, Part B, of Regulation 309, as a hazardous waste chemical. Hazardous waste chemicals include chemical products or manufacturing intermediates that, from time to time, may be off-specification or otherwise unacceptable for use.

This proposed listing is based on the following considerations:

> 2-Nitropropane exhibits the hazardous characteristic of ignitability. It is also a recognized carcinogen in laboratory animals. In particular, this chemical has been shown to cause heptocellular carcinomas and hepatic adenomas in rats. It is also a suspected carcinogen in humans (details of toxicity are presented in Section 4.5). Its mobility and moderate persistence in ground water are additional concerns.

If wastes contaminated with 2-nitropropane are mismanaged either in handling, transportation or disposal, the chemical could enter the environment and create a hazard.

1.2 Listing under other Canadian legislation

Under the federal Transportation of Dangerous Goods Act (TDGA), 2-nitropropane (with a flash point of 37.8°C for pure chemical) is classified as a flammable liquid (Class 3.3, flash point between 23°C and 61°C, identified as moderately flammable for international air transport and international marine transport of waste). The chemical is also listed as a dangerous good in Schedule II, List II (Class 9.2). The used chemical is still considered a dangerous good under TDGA.

1.3 Listing under U.S. legislation

2-Nitropropane waste has been listed in the U.S. "Resource Conservation and Recovery Act" (RCRA) as a hazardous waste if disposed of as a spent solvent or as still bottoms from the recovery operation of that solvent (see appendix A). Spent solvent has been defined in the U.S. legislation as follows:

a) the original chemical mixture must be used for its solvent properties (i.e. it dissolves or mobilizes constituents);

b) the chemical mixture must be spent;

c) before use (i.e. at the commercial stage) the chemical mixture must have a total concentration of 10 percent or more of the listed solvents.

In addition, 2-nitropropane is listed as a hazardous waste chemical when discarded as commercial chemical products, off-specification species, container residues and spill residues.

2.0 DESCRIPTION OF INDUSTRIAL SECTOR

2-Nitropropane is a solvent used mostly in ink applications. The industrial sectors responsible for generation of wastes contaminated with 2-nitropropane include the sector producing the chemical, the sector using 2-nitropropane as an intermediate to produce other chemicals, and any other sectors using solvents or reagents containing 2-nitropropane.

2.1 Production of 2-Nitropropane

2-Nitropropane is not produced in Canada (Edwards, 1988). The production process used in the United States involves the vapour phase reaction of nitric acid with excess propane, in a reactor chamber at 370 to 450°C and under a pressure of 8 to 12 atmospheres. The reaction product, which must be further processed and distilled, is a mixture of nitromethane, nitroethane and 1- and 2-nitropropanes. The composition, depending on the reaction temperature, has typically the following distribution (IARC, 1982):

nitromethane:	20%
nitroethane:	8%
1-nitropropane:	18%
2-nitropropane:	46%

The USEPA (1985a) listed Angus Chemical Co. (Sterlington, LA) and W.R. Grace Co. (Deer Park, Tx) as the only U.S. producers. Trakinas (1988), in a personal communication, has indicated that W.R. Grace Co. does not export into Canada. Edwards (1988), of Van

Waters & Rogers Ltd. (the sole distributor of 2-nitropropane in Canada for Angus Chemical Co.), has indicated that the sales figures in Ontario are as follows:

1986:	32,000 kg
1987:	26,000 kg
1988:	6,100 kg
1989:	606 kg

The low sales figures in 1988 and 1989 are an indication of the decrease in exportation to Canada from Angus Chemical Co. In addition, Van Waters & Rogers Ltd. confirmed that they will not sell 2-nitropropane any more (Edwards, 1990).

2.2 Use in the chemical industry

In the chemical industry, 2-nitropropane can be used either as a chemical intermediate or as a solvent. As an intermediate, 2-nitropropane is used to produce 2-nitro-2-methyl-1-propanal and 2-amino-2-methyl-1-propanol. As a solvent, it is used to separate closely related materials in natural products or in reaction mixtures, and as a medium for chemical reactions (Baker et al., 1981). For example, oleic acid is difficult to separate from poly-unsaturated fatty acids, but can be crystallized out at between minus 25 and minus 40°C in 2-nitropropane. Similarly cetyl and oleyl alcohols can be separated with nitropropane at room temperature.

In Ontario, 2-nitropropane is not used in the chemical industry (at least not in quantity worth reporting by Statistics Canada or other industrial associations).

2.3 Use as a solvent/reagent

2-nitropropane is used as a solvent for products such as coatings, inks and adhesives. The chemical is blended with other solvents to obtain some desired property of the products (e.g. greater solubility, improved drying time, or lower resistivity in electro-static coatings). Over the last years, 2-nitropropane has been gradually phased out from different sections of the industry, due to the increase awareness of its toxicity in the working place. Since 1988, 2-nitropropane has been exclusively used in the ink formulation industry in Ontario (Edwards, 1988).

2.3.1 Production and use of printing ink

Ink consists of colouring material (a dye or pigment) dispersed in a base which may be an oil, solvent or water. Flexographic and gravure inks may contain 2-nitropropane as an additive to modify drying rates in solvent and water based formulations. In 1984, flexographic and rotogravure inks represented 16% and 12%, respectively, of a total ink sale of 57,502 tonnes (Statistics

Canada, 1985). The Ontario printing ink establishments, reporting to Statistics Canada (1986), are presented in Table 1.

The Generator Registration Reports (GRR, 1989), filed by the printing ink establishments reported in Table 1, were reviewed. The information provided indicates that the major sources of waste are off-specification batches and spent solvent. The spent solvent consists of equipment cleaning wastes and still bottoms from the recovery of the solvent. Other wastes are rinse water from equipment cleaning and wastewater treatment sludge.

Printing shops produce spent solvent from cleaning operations and condensate from solvent vapour recovery. The solvent enters the printing press as a component in the ink and as a cleaning solvent between runs. Some quantity of solvent, usually the base solvent, is added to the ink at the press for proper ink consistency. Most of the solvent evaporates at the press. In the larger printing shops, recovery of the solvent vapour is usually done by carbon absorption followed with distillation to produce a condensate. Typically 17% of the solvent used is recovered from solvent vapour.

3.0 WASTE MANAGEMENT PRACTICES

3.1 Waste Generation

As indicated in Sections 2.1 and 2.2, 2-nitropropane is not produced in Canada nor is it used in Ontario in the chemical industry. In 1988, 2-nitropropane has been exclusively used in the ink formulation industry (Edwards, 1988).

3.1.1 Ink production and use

The amount of waste generated from the manufacturing and use of ink is estimated from generation factors developed by USEPA (1985b):

1) spent solvent and recovery still bottoms are generated at a rate of 0.047 kg per kg of ink produced; the quantities of spent solvent and still bottom are approximately equal (i.e. the generation rate of spent solvent alone is 0.0235 kg per kg of ink produced);

2) off-specification products are generated at a rate of 0.018 kg per kg of ink produced.

For ink based on 2-nitropropane, the solvent typically represents 28% of the total volume of ink. This figure is derived from a reported range of 23 to 30% (Whittenberg, 1988).

The amount of ink produced from 2-nitropropane in Ontario is based on the 1987 sales figure of 2-nitropropane (see Section 2.1) and the typical concentration of 2-nitropropane in ink. The production

of ink (2-nitropropane based) is estimated at 92,857 kg (26,000/0.28).

The annual generation of spent solvent and still bottoms (from production and use of ink) is based on the generation rate and the estimated ink production in 1987, i.e. 4,364 kg (92,857x0.047).

Similarly, the annual generation of off-specification products is estimated to be 1,671 kg (92,857x0.018).

The spent solvent is expected to contain near 75% 2-nitropropane, while the still bottoms are expected to contain near 10% and the off-specification products an estimated concentration of 15% (USEPA, 1985b). Thus a total of 2.2 tonnes of 2-nitropropane could be released annually to the environment, if the above wastes were mismanaged. It is to be noted that the quantity of 2-nitropropane in waste will decrease with the drop in the use of this solvent. For example, the total release of 2-nitropropane is estimated at 0.5 tonne in 1988, and 0.05 tonne in 1989.

3.2 Waste management

Management of waste containing 2-nitropropane such as cleaning waste, and off-specification products from paint and ink formulation, includes contract hauling to landfill, incineration, burning in boilers, discharge to wastewater, and solvent recovery (USEPA, 1985b).

Data from the Ontario Generator Registration Reports (GRR, 1989) indicate that the majority of the hazardous wastes from the paint and ink formulation industry are disposed of as regulated wastes under Regulation 309.

4.0 HAZARDOUS PROPERTIES OF THE WASTE

4.1 Hazardous properties

In a spent solvent, 2-nitropropane is typically present at concentrations ranging from 50 to 90 percent. In the still bottoms from recovery operation, this solvent is present at concentrations ranging from 1 to 20 percent (USEPA, 1985b). Taking the worst case concentration of 50 to 90%, the waste toxicity can be evaluated in terms of toxicity found for 2-nitropropane.

4.2 Hazardous characteristics

Based on Regulation 309 definitions, 2-nitropropane exhibits one (i.e. ignitability) of the four hazardous characteristics: ignitability, reactivity, corrosivity and leachate toxicity. Depending on the concentration of 2-nitropropane (and other ignitable constituents) in a waste, the waste may also be

ignitable. Ignitability remains a secondary characteristic compared to the toxicity of 2-nitropropane, specially at low concentrations.

4.3 Physical and chemical properties

Selected physical and chemical properties of 2-nitropropane are presented in Table 3.

4.4 Environmental behaviour

4.4.1 Environmental mobility

Environmental mobility refers to the multimedia partitionning in this paragraph. Using the Fugacity Model (Level 1) (Mackay et al, 1982), it is estimated that 66.3% of 2-nitropropane would be in the water medium and 33.6% in air. Since the expected dispersion is in two media, the concern level for environmental mobility is high.

4.4.2 Persistence

2-Nitropropane will readily burn if ignited (flash point of 39 °C), but it does not ignite spontaneously. Because 2-nitropropane does not absorb visible light, it will not directly photolyze in the lower atmosphere or surface water. According to USEPA (1985b), "2-nitropropane can be attacked by hydroxyl radicals in the upper atmosphere".

Several studies have shown that soil bacteria or their cell-free extracts could degrade 2-nitropropane (USEPA, 1985). However, the significance of microbial degradation in the natural environment is unclear.

Although 2-nitropropane is expected to degrade through hydroxyl radical oxidation in the troposhere and biodegradation in water, these processes are expected to be slow (USEPA, 1985b).

Because of the relatively low level of biological activity in ground water, 2-nitropropane can be considered as moderately persistent (US Federal Register, 1985).

4.4.3 Bioaccumulation

Based on a log octanol/water ratio of 0.65, a calculated bioconcentration factor (BCF) of 1.8 is derived using the relationship developed by Veith (1980). It is expected that bioaccumulation in aquatic organisms would not be significant.

4.4.4 Environmental Exposure

Most of the waste containing 2-nitropropane and generated in Ontario is landfilled in secure landfill or incinerated. Mismanagement and improper disposal could result in substantial adverse health and environmental effects.

In a scenario of mismanagement at a landfill site, volatilization of the solvent could create an air pollution problem. In addition, exposure through contamination of ground water is possible.

Since 2-nitropropane has a high water solubility of 17.2 g/L, leaching from a contaminated waste would be likely. It is also expected that, with an estimated soil absorption coefficient (K_{oc}) of 20, it will not be attenuated in a ground water aquifer. The log octanol/water partition coefficient (K_{ow}) of 0.65 suggests that 2-nitropropane is mobile in a water medium (Briggs, 1973).

Because of the accepted mobility and "moderate persistence" (U.S. Federal Register, 1985) of 2-nitropropane, it is expected that it can reach the environmental receptors in harmful concentrations (US Federal Register, 1986).

In the U.S., the Land Disposal Restrictions of the Hazardous and Solid Waste Amendments (HSWA) of 1984 restricts disposal of listed hazardous wastes in landfills. Similarly in Ontario, wastes listed or classified as hazardous under Regulations 309 must be disposed of at waste management sites licensed by the Ministry of the Environment for such wastes.

4.5 Toxicity

4.5.1 Acute lethality

According to Proctor et al. (1988), 2-nitropropane is a pulmonary irritant in animals and it is expected that severe exposure will cause the same effect in humans. The LC_{50} (6-hour inhalation exposure) in male Sprague-Dawley rats was reported to be 400 ppm (1460 mg/m^3); female rats were less sensitive (Lewis et al., 1979). The LD_{50} (intraperitoneal) in mice was determined to be 75 mg/kg (RTECS, 1988). Curtis and Ward (1981) attempted to determine the acute 96-hour LC_{50} of 2-nitropropane in the fathead minnow, Pinnephales promelos, and they found no mortality at 612.5 ppm, the highest concentration tested.

4.5.2 Sublethal effects, plants

Data regarding sublethal effects on plants were not found in the available literature (RTECS, 1988; TOXNET, 1988).

4.5.3 Sublethal effects, mammals

Rats exposed to 207 ppm of 2-nitropropane by inhalation for 24 weeks developed considerable liver damage (Lewis et al., 1979). There was an increase in the weight of the liver and in the number of lesions which were considered to be preneoplastic.

In a 22-month inhalation experiment by Griffin et al. (1980, 1981) where rats were exposed to 2-nitropropane at 25 ppm, all parameters of blood chemistry and morphology remained normal. Body and organ weights were also normal. Exposure at higher doses of up to 200 ppm produced an increase in liver weight.

According to Proctor et al. (1988), workers exposed to 30 to 300 ppm of 2-nitropropane complained of irritation of the respiratory tract.

4.5.4 Sublethal effects, non-mammalian

Data regarding sublethal effects on non-mammals were not located in the available literature (RTECS, 1988: TOXNET, 1988).

4.5.5 Teratogenicity

Developmental abnormalities were observed in the fetuses of rats when the rats were injected intraperitoneally with 170 mg/kg of 2-nitropropane during gestation days 1-15. (Hardin et al., 1981). Fetotoxicity was observed in the absence of maternal toxicity.

4.5.6 Mutagenicity

2-Nitropropane gives positive results for various in-vitro assays including human lymphocytes. However in-vivo tests were negative (Sax, 1984; RTECS, 1988; TOXNET, 1988). IARC (1982) has concluded that 2-nitropropane is mutagenic to Salmonella typhimurium. Chromosomal abberations were detected in human lymphocytes when the cell cultures were exposed to 2-nitropropane.

In a recent study on female mice (Dayal et al., 1989), a dose of 6.7 mmol/kg 2-nitropropane was sufficient to cause hepatotoxicity. Additional tests on Salmonella typhimurium (strains TA98, TA100 and TA102) showed that 2-nitropropane was mutagenic.

A variety of genetic endpoints in mammalian cells, including DNA repair synthesis, micronuclei induction, and point mutations at the HGPRT locus have been detected both in cell culture and in whole animals (George et al., 1989; Roscher et al., 1990). However, the induction of mutagenic lesions in mammalian systems appears to be organ-specific (liver), and may be dependent on the induction of specific enzyme bioactivation pathways in the target organ.

4.5.7 Carcinogenicity

Rats exposed to 2-nitropropane vapour doses of up to 207 ppm daily for 6 months developed hepatic neoplasms and hepatocellular hyperplasia (Lewis et al., 1979).

IARC (1982) has concluded that there is sufficient evidence for the carcinogenicity of 2-nitropropane in laboratory animals. It has been shown to cause liver cancer and hepatic adenomas (IARC, 1982). The American conference of Governmental Industrial Hygienists also has designated 2-nitropropane as an industrial substance suspected of having carcinogenic potential in human (ACGIH, 1981).

4.6 Results of Vector Scoring

A vector scoring system for waste categorization and review has been developed to evaluate the toxicity and exposure of waste to human health and the environment. The results of the Vector Scoring for 2-nitropropane are shown in Table 4. Details of the scoring procedure are presented in the guidance manual (MOE, 1991).

The carcinogenic properties of 2-nitropropane are the main concern for health effects. The compound has been shown to cause liver cancer in laboratory animals. Mobility and persistence are the main concerns from an environmental perspective. Leaching to ground water and contamination of drinking water are highly probable, if discharged to the environment in an uncontrolled manner.

The justification for the individual score is presented in Appendix B.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Based on an annual use of 26.0 tonnes of 2-nitropropane in Ontario (1987), spent solvent (containing 2-nitropropane) is generated at 2.2 tonnes/year, and off-specification products at 1.7 tonnes/year (see Table 2). The quantity of still bottoms from solvent recovery is estimated at 2.2 tonnes. This volume of waste represents a total of 2.2 tonnes of 2-nitropropane, which could adversely affect the environment if the waste was mismanaged.

Based on the 1989 use of 2-nitropropane (i.e. 606 kg, from Section 2.1), the volume of waste generated in 1989 represents a total of 51 kg of 2-nitropropane (i.e. 2,200 kg x (606 kg/26,000 kg)).

Because of 2-nitropropane mobility and persistence in the environment and because 2-nitropropane has carcinogenic potential in humans, a serious potential hazard is presented by its release to the environment. These considerations justify that 2-nitropropane be listed in Schedule 1 of Regulation 309 (see Appendix C).

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TABLE 1: Ontario printing ink formulation establishments reporting to Statistics Canada

* BCM Inks Ltd., Brampton
* CFC Liquid Inks Ltd., Etobicoke
* Canadian Fine Colours Co. Ltd., North York
* Canadian Fine Colours Co. Ltd., London
* Converters Ink (Canada) Ltd., North York

* General Printing Ink Corporation, North York
* General Printing Ink Corporation, Burlington
* Hostmann-Steinberg Canada Ltd., Scarborough
* Immont Canada Inc., (Graphics Group), Scarborough
* Immont Canada Inc., (Graphics Group), Toronto

* Immont Canada Inc., (Peters St-Graphics Group), Brampton
Immont Canada Inc., (Graphics Group), London
Inter-Provincial Inks Ltd., Vaughan
Johnson & Bloy Canada Inc., Mississauga
* Lester Ink & Chemicals Ltd., Markham

Naz-Dar Canada Ltd., York
* PPG Canada Inc. (Bowers Printing Ink Div.), Markham
* Reiger Flexo & Gravure Ltd., North York
* Reiger Printing Ink Co. Ltd., Nepean
* Reiger Printing Ink Co. Ltd., Toronto

Reiger Printing Ink Co. Ltd., Burlington
Reiger Printing Ink Co. Ltd., London
* Sinclair Valentine-Frye Ltd., North York
* Sinclair Valentine-Frye Ltd., London

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* : establishments which have submitted a Generator Registration Report, and disposed of their hazardous wastes under Regulation 309 requirements.

Source: Statistics Canada, 1986, SIC #3791

TABLE 2: Estimated 1987 generation of 2-Nitropropane waste in Ontario (1)

PROCESS	WASTE (tonnes)	2-NITROPROPANE CONCENTRATION	2-NITROPROPANE (tonnes)
Spent solvent	2.2	75 %	1.7
Still bottoms	2.2	10 %	0.2
Off-specification products	1.7	15 %	0.3
TOTAL:	6.1	--	2.2

(1) Based on 1987 sales of 2-nitropropane in Ontario (i.e. 26 tonnes) which was used exclusively in ink formulation (containing typically 28% solvent). Emission factors are based on figures derived by USEPA (1985b) listing document.

TABLE 3: Properties of 2-nitropropane

Chemical Abstract #	: 79-46-9
Chemical Abstact Name	: Propane,2-Nitro
Synonyms	: Dimethylnitromethane, Isonitropropane 2-NP
Trade Names	: NiPar S-20 Solvent NiPar S-30 Solvent
Chemical Formula	: $C_3H_7NO_2$
Molecular Weight	: 89.1
Boiling Point	: 120.3°C
Melting Point	: -91.3°C
Density	: 0.988 g/cc. at 20°C
Solubility	: 17000 ppm at 25°C
Volatility	: vapor pressure 13mm at 20°C
Flash Point (open cup)	: 37.8°C
Conversion Factor (in air)	: 1ppm = 3.65 mg/m^3

TABLE 4: Results of vector scoring of 2-nitropropane

Parameter	Score	Concern Levels(1)
1. Environmental Mobility	10	≥ 7
2. Environmental Persistence	*	≥ 7
3. Bioaccumulation	0	≥ 7
4. Environmental Exposure	7	≥ 7
5. Acute lethality	4	≥ 6
6. Sublethal effects plants	N/D	≥ 4
7. Sublethal effects mammals	4	≥ 4
8. Sublethal effects non-mammals	N/D	≥ 4
9. Teratogenicity	2	≥ 2
10. Mutagenicity	8	≥ 6
11. Carcinogenicity	10	≥ 2

(1): concern levels established for the listing of hazardous wastes (a score above the concern level indicates that the contaminant is toxic and mobile enough to justify its listing in Regulation 309).

N/D: no data available.

* considered to be moderately persistent however no half life data available in water.

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Appendix A: U.S. Regulations

The USEPA has defined spent solvents as those solvents that are used for their "solvent" properties, that is to solubilize (dissolve) or mobilize other constituents (for example, solvents used in degreasing, cleaning, fabric scouring, as diluents, extractants, reaction and synthesis media). A solvent is considered "spent" when it has been used and is no longer fit for use without being regenerated, reclaimed or otherwise reprocessed.

The listing of spent solvents was originally drafted with the intention to include technical grade or pure forms of the solvent. Effective December 31,1985 the listed solvents were to include mixtures containing ten percent or more total listed solvents. The ten percent threshold applied to solvent mixtures, before use. The agency took this position based on data which indicate that solvent mixtures, commercialy used, typically contain more than ten percent total solvents.

Source: U.S. Federal Register, Final Rule, Vol. 51, Feb. 25, 1986, p. 6537-6542.

Appendix B: Justification for Vector Scores of 2-Nitropropane

Parameter	Score	Justification
1. Environmental Mobility	10	Using the level 1 fugacity model 33.2% in air and 66.3% in water
2. Environmental Persistence	--	Considered moderately persistent by U.S. EPA., however no half life data in water.
3. Bioaccumulation	0	Calculated BCF of 1.8
4. Environmental Exposure	7	Because of easy pathway between the contaminant sources and receptor
5. Acute lethality	4	LC_{50} = 1460 mg/m^3 (400ppm) (Inhalation)
6. Sublethal effects plants	N/D	no data
7. Sublethal effects mammals	4	No effect on rats at 25 ppm (91 mg/m^3) for a 22 month inhalation test.
8. Sublethal effects non-mammals	N/D	No data
9. Teratogenicity	2	Delayed development of the heart in rat pups
10. Mutagenicity	8	Mutagenic to Salmonella typhimurium.
11. Carcinogenicity	10	Considered a potential human carcinogen by ACGIH.

N/D: no data available.

Appendix C: Proposed Amendment to Regulation 309

Schedule 1, NA9305

"The following spent non-halogenated solvents: toluene, methyl ethyl ketone, carbon disulphide, isobutanol, pyridine, and **2-nitropropane**, and still bottoms from the recovery of these solvents."

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